

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY


(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference 2003B137	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/EP2004/014477	International filing date (<i>day/month/year</i>) 16.12.2004	Priority date (<i>day/month/year</i>) 18.12.2003	
International Patent Classification (IPC) or national classification and IPC INV. C07C45/50 C07C29/141			
Applicant EXXONMOBIL CHEMICAL PATENTS INC.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 5 sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 18.10.2005		Date of completion of this report 24.03.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized officer Kardinal, S Telephone No. +31 70 340-3483	



INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/014477

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-32 as originally filed

Claims, Numbers

1-32 received on 18.10.2005 with letter of 18.10.2005

Drawings, Sheets

1/2, 2/2 as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/014477

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-29,32
	No: Claims	30-31
Inventive step (IS)	Yes: Claims	1-29
	No: Claims	30-32
Industrial applicability (IA)	Yes: Claims	1-32
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V.

1. Amendments

The amendments of claims 1 and 18 filed with the letter dated 18.10.05 are based on page 1, lines 5-6, page 20, lines 7-9 and page 24, lines 7-11 of the application as filed and comply with Article 34(2)(b) PCT.

2. Reference is made to the following documents :

- D1: GB 643 503 A (BATAAFSCHE PETROLEUM) 20 September 1950
- D2: DE 100 35 120 A (BASF AG) 25 January 2001
- D3: EP-A-0 188 246 (UNION CARBIDE CORP) 23 July 1986
- D4: US-A-3 868 422 (HAGEMEYER JR HUGH J ET AL) 25 February 1975
- D5: US-A-3 188 351 (HANS LEMKE) 8 June 1965
- D6: DE 102 27 995 A (OXENO OLEFINCHEMIE GMBH) 25 September 2003

3. Novelty

3.1 Document D1 discloses (cf. the passages indicated in the international search report) a process for the production of alcohols by high pressure hydroformylation of olefins and subsequent hydrogenation of the hydroformylation product.

The hydroformylation (D1: first stage) takes place in two hydroformylation reactors (Fig. 3: 4, 14). The hydroformylation products are fed to a high pressure separator (Fig. 3: 20). Unreacted gases from the hydroformylation and unreacted hydrogen from the subsequent hydrogenation reaction, which takes place in a second (Fig. 3: 25) and third stage (Fig. 3: 35), are recycled to the first and second reactor of the hydroformylation stage (Fig. 3: 15->16->17->10->12->13 and 38->32->27->22->16->17->10->12->13) .

The partial pressure of carbon monoxide in the offgas (Fig. 3: 15,21) from the high pressure separator is not disclosed.

3.2 Document D2 discloses (cf. the passages indicated in the international search

report) a process for the production of aldehydes and alcohols by high pressure hydroformylation of olefins.

The hydroformylation takes place in two hydroformylation reactors (Fig. 1: **1**, **2**). The hydroformylation products are fed to a high pressure separator (Fig. 1: **3**) and unreacted gases from the hydroformylation are recycled to the first and second reactor of the hydroformylation stage.

The partial pressure of carbon monoxide in the offgas from the high pressure separator (Fig. 1: **3**) is not disclosed.

3.3 Document D3 discloses (cf. the passages indicated in the international search report) a hydroformylation processes using two reactors (Fig. 2: **50-52**, **80**). The hydroformylation product is fed to a separator (Fig. 2: **66**) and offgas (Fig. 2: **68**) is recycled back to the first and second reactor (Fig. 2: **66->74**, **66->70**).

A partial pressure of carbon monoxide in the offgas (Fig. 2: **66**) of more than 75 barg is not disclosed.

3.4 The process according to claim 1 of the present invention differs from these known hydroformylation reactions in that the carbon monoxide content of the offgas from the high pressure separator is such that the partial pressure of carbon monoxide is above 75 barg.

The subject-matter of claims 1-29 is therefore novel (Article 33(2) PCT).

3.5 The document D1 furthermore discloses (cf. Fig. 3) an apparatus for the production of alcohols from an olefin comprising the following parts :

- a series of two reactors (**4**, **14**) suitable for catalytic hydroformylation of olefin
- means (**46**) which are as such suitable for the removal of catalyst residues from the hydroformylation product
- a reactor (**35**) which is suitable for hydrogenating a hydroformylation product from which catalyst residues have been removed and
- means (**38->32->27->22->16->17->10->12->13**) suitable for recycling unreacted hydrogen from the hydrogenation reactor (**35**) to the second hydroformylation

- reactor (14) and furthermore
- means (Fig. 3: 15->16->17->10->12->13) suitable for recycling unreacted gases from the hydroformylation reaction.

The subject-matter of claims 30 and 31 is therefore not novel (Article 33(2) PCT).

3. Inventive Step

3.1 Any of the documents D1 or D2 could be regarded as representing the closest prior art to the subject-matter of independent claim 1.

The difference between the process of claim 1 and the closest prior art is the partial pressure of carbon monoxide in the offgas of at least 75 barg.

The problem to be solved may be regarded as avoiding cobalt plating in the hydroformylation reactor (see page 24, lines 10-11) of the application.

The subject-matter of claims 1-29 of the present application can be considered as involving an inventive step (Article 33(3) PCT) as the problem of cobalt plating of the hydroformylation reactor is not addressed by the prior art (D1-D6) and the solution of the problem by maintaining a partial pressure of carbon monoxide in the offgas of at least 75 barg was not obvious.

However, it is clear from the above that the use of a cobalt catalyst is essential to the definition of the invention and since independent claim 1 does not contain this feature it does not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT that any independent claim must contain all the technical features essential to the definition of the invention.

3.2 Duplex stainless steel is a known pressure resistant material and the skilled person would use it in an apparatus of D1 according to the circumstances when necessary.

The subject-matter of claims 32 of the present application does therefore not involve

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/EP2004/014477

an inventive step (Article 33(3) PCT)

2003B137

33

CLAIMS

1. A process comprising the hydroformylation of one or more olefins with carbon monoxide and hydrogen to form a hydroformylation product, wherein the hydroformylation takes place in a series of at least two hydroformylation reactors, wherein unreacted gases from hydroformylation or a subsequent process stage are recycled to at least the hydroformylation reactor in the second position, whereby the hydroformylation product is fed to a high pressure separator, and wherein the carbon monoxide content of the offgas from the high pressure separator is such that the partial pressure of carbon monoxide is above 75 barg.
2. The process according to claim 1 comprising a stage for hydrogenating the hydroformylation product to form alcohols, which process comprises catalytically hydroformylating the olefin(s), removing catalyst residues from the hydroformylation product to form a substantially catalyst-free hydroformylation product, and subsequently hydrogenating the substantially catalyst-free hydroformylation product, wherein the unreacted gases that are recycled comprise unreacted hydrogen from the hydrogenation stage.
3. The process according to claim 2 wherein the unreacted gases that are recycled comprise unreacted gases from the hydroformylation reaction and unreacted hydrogen from the hydrogenation stage.
4. The process according to any of the preceding claims wherein the hydroformylation is a high or medium pressure hydroformylation process in which the olefin(s) are reacted with carbon monoxide and hydrogen in the presence of a hydroformylation catalyst, wherein feed to the first reactor comprises a mixture of:
 - i. olefin(s)
 - ii. carbon monoxide
 - iii. hydrogen
 - iv. recycle gases comprising unreacted gaseous materials from the hydroformylation reaction;

2003B137

34

and the feed to the reactor in the second position comprises a mixture of:

- i. the reaction product from the first reactor
- ii. recycle gases comprising unreacted gaseous materials from the hydroformylation reaction.

5. The process according to claim 4 in which the hydroformylation is performed in a series of at least three reactors and the feed to the reactor in the third position comprises:

- i. the reaction product from the reactor in the second position
- ii. recycle gases comprising gaseous materials from the hydroformylation reaction.

6. The process according to claim 4 or 5 in which the hydroformylation is performed in a series of four reactors and the feed to the reactor in the fourth position consists of the reaction product from the reactor in the third position.

7. The process according to any of the preceding claims in which the hydroformylation is performed at a pressure of from 50 to 350 barg, preferably 250 to 350 barg, most preferably from 275 to 325 barg.

8. The process according to any of the preceding claims in which the hydroformylation is performed at a temperature of from 120 to 185°C, preferably from 170 to 180°C.

9. The process according to any of the preceding claims employing a hydroformylation catalyst, in which the catalyst supplied is absorbed in the olefin feed.

2003B137

35

10. The process according to any of the preceding claims employing a hydroformylation catalyst which comprises a rhodium catalyst or a cobalt catalyst, particularly those selected from hydrocobaltcarbonyl or rhodiumcarbonyls.
11. The process according to claim 10 in which the catalyst is a cobalt catalyst and the molar ratio of hydrogen to carbon monoxide in the syngas used for hydroformylation is about 1.3:1.
12. The process according to claim 10 or 11 in which the catalyst is a cobalt catalyst and the hydroformylation product is purified by injection of caustic soda and/or sodium carbonate into the hydroformylation reaction product in a decobalter vessel.
13. The process according to claim 12 in which a stoichiometric excess of 100 to 200%, particularly 140 to 180% of sodium hydroxide or carbonate is used.
14. The process according to claim 12 or 13 in which the decobalter is operated at a temperature in the range 155-165°C.
15. The process according to claim 10 or 11 in which the catalyst is a cobalt catalyst, and the cobalt is removed by an acidic and/or oxidative method.
16. The process according to claim 15 wherein the acidic method uses formic and/or acetic acid.
17. The process according to claim 15 or 16 wherein the oxidative method uses oxygen, an oxygen containing gas, or air.
18. The process according to any of the preceding claims wherein the partial pressure of carbon monoxide is above 77 barg.

2003B137

36

19. The process according to claim 18 in which the high pressure separator operates at a pressure of 250 barg or higher, preferably a pressure in the range 250 to 300 barg, more preferably 260 to 270 barg.

20. The process according to claim 18 or 19 in which the quantity of high pressure gas required for recycle is sent to an offgas recycle compressor system.

21. The process according to any of claims 18 to 20 in which the liquid left in the high pressure separator is fed to an intermediate pressure separator where the pressure is reduced to a level at which gases dissolved or entrained in the liquid from the high pressure separator are released as an intermediate pressure offgas.

22. The process according to claim 21 in which the pressure in the intermediate pressure separator is between 80 and 120 barg, preferably between 90 and 110 barg.

23. The process according to claim 21 or 22 in which at least a portion of the intermediate pressure offgas is sent to an offgas recycle compressor system for subsequent recycle.

24. The process according to any of the preceding claims in which the recycle employs a compressor system comprising a series of gas compressor stages in which the pressure is gradually increased to the pressure required in the hydroformylation reaction.

25. The process according to claim 24 in which the recycle compressor system comprises three gas compressor stages in series.

26. The process according to claim 25 in which high pressure offgas and intermediate pressure offgas from the hydroformylation step are fed (together with unreacted gas from the hydrogenation stage, when present) to the first compressor stage which preferably operates at a suction pressure between 50 and 60 barg.

2003B137

37

27. The process according to claim 26 in which the gas mixture discharged from the first compressor stage is fed, optionally with intermediate pressure offgas, to the second compressor stage where the pressure is increased to within the range 140 to 180 barg, preferably 150 to 170 barg.

28. The process according to claim 27 in which the gas mixture discharged from the second compressor stage is fed, optionally with high pressure offgas, to the third compressor stage.

29. The process according to any of the preceding claims wherein duplex stainless steel is used as material of construction for at least one piece of the hydroformylation reactors or any of their associated equipment.

30. An apparatus for the production of alcohols from an olefin, comprising a series of at least two reactors for catalytic hydroformylation of olefin, means for the removal of catalyst residues from the hydroformylation product, a reactor for hydrogenating the hydroformylation product from which catalyst residues have been removed, and means whereby unreacted hydrogen from the hydrogenation reactor is recycled to at least the second hydroformylation reactor.

31. The apparatus according to claim 30 which comprises both means for recycling unreacted hydrogen from the hydrogenation reactor, and means for recycling unreacted gases from the hydroformylation reaction.

32. The apparatus according to claim 30 or 31 wherein duplex stainless steel is used as material of construction for at least one piece of the hydroformylation reactors or any of their associated equipment.